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A review of thermochemical conversion of microalgae

A. Marcilla, L. Catalá*, J.C. García-Quesada, F.J. Valdés, M.R. Hernández

Department of Chemical Engineering, University of Alicante, Apdo. 99, San Vicente del Raspeig E-03080, Alicante, Spain

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ABSTRACT

Microalgae are very effective microorganisms for CO_2 capturing and a promising source of lipids for biodiesel as well as other interesting compounds. Many different ways of exploitation of these organisms are being tested. This work presents a review of the state of the art of the research and development of thermochemical conversion of microalgae with a special focus on pyrolysis and hydrothermal liquefaction. Aspects related to the type of reactors, the products obtained and the analytical applications are covered. The actual reaction scheme of pyrolysis of microalgae is extremely complex because of the formation of over hundreds of intermediate products. Various kinetic models reported in the literature and in a previous study with experimental validations are presented in this review to provide the current status of the study.

Contents

1. Introduction

Energy is the fundamental driving force of the economic growth and the world's development in addition to the material basis for human life. In recent years, the rapid development of the world economy has led to the global shortage of fossil fuels so that their prices have increased significantly. Moreover, the use of fossil fuels has also brought a very prominent environmental problem. Therefore, accelerating the development and utilization of new energy sources has become a common action around the world.

Generally, microalgae contain varying amounts of lipids, sugars, proteins and pigments among other compounds. Presently, the conversion of microalgae to fuel products mostly focuses on the lipid fraction, which can be used to produce high-quality biodiesel

* Corresponding author. Tel.: +34 965 90 3400x2386; fax: +34 965 90 3826.
E-mail address: lucia.catala@ua.es (L. Catalá).

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by the conventional esterification and transesterification. However, after lipid extraction from microalgae cells, large amounts of microalgae residues, which may contain mainly soluble polysaccharides, proteins and some residual lipids, are disposed or alternatively used as animal feed. However, diversified biofuels production from microalgae is necessary to improve the overall energy balance. One of the successful examples is the utilization of microalgae biomass (after lipid extraction) for bioethanol production, since high concentrations of carbohydrates are still present in the biomass. Other potential biofuels that can be derived from the microalgae biomass residues are, such as bio-oils from pyrolysis or hydrothermal process. This is a likely strategy to re-utilize the waste to produce another source of energy which greatly amplifies the sustainability of microalgae biofuels [1].

Hydrothermal liquefaction is one of the alternatives being increasingly considered, especially at low temperatures and pressures near the water critical pressure [2–5]. Pyrolysis has been widely studied as an alternative to obtain valuable products and fuels from different feedstocks, mainly municipal, plastic and lignocellulosic wastes. This technique could be applied to the residue obtained after lipid extraction or directly to the algae.

Pyrolysis could also have a great potential for the characterization of the microalgae and it could be used as a rapid test to obtain a tentative estimation of the biochemical composition. In this sense, TG (thermogravimetric analysis), TG-IR(thermogravimetric analysis-infrared spectroscopy) and Py-GC/MS (pyrolysis-gas chromatography/mass spectroscopy) are powerful analytical techniques [6–12]. On the other hand, the design of the equipments for the thermochemical processing, models describing the kinetics and the governing mechanisms are required [13]. Thermogravimetric analysis is broadly used to understand these pyrolytic characteristics [14] and mainly to determine the kinetic parameters [15–18].

Extensive literature has been published on the experimental and mechanistic aspects of lignocellulosic biomass [19–23]. Very little information is available on pyrolysis kinetics of microalgae [24–27], but the kinetic models used to describe the pyrolysis behaviour are not always correctly applied [28].

The overall objectives of this review are: to present an updated revision of the state of the art in the field of experimental and theoretical (mathematical modeling and simulation) aspects associated with pyrolysis of microalgae and to bring out clearly the current status of research in the field of their hydrothermal liquefaction.

Specifically, aspects related to the type of reactors and conditions employed, the products obtained and the analytical applications are considered. Various kinetic models reported in the literature and in a previous study with experimental validations are presented in this review to provide the current status of the study and to show that the kinetic analysis is not always correctly applied, because isoconversional methods are used in processes that clearly occur in more than one stage.

2. Pyrolysis

Nowadays, pyrolysis of biomass is an alternative that has been widely investigated. The pyrolysis typically refers to a process by which the biomass is thermally degraded at moderate temperatures (350–700 °C) in absence of oxygen. It produces solid, liquid and gaseous products. These products are of interest, as they are likely alternate sources of energy and/or chemicals. As a consequence, the study of pyrolysis has been gaining increasing importance.

2.1. Operating conditions

Depending on the operating conditions, the pyrolysis process can be divided into three subgroups: slow pyrolysis, fast pyrolysis and flash pyrolysis (Table 1).

2.1.1. Slow pyrolysis

Slow pyrolysis is defined as the pyrolysis that occurs under a heating rate range of 0.1 and 1 °C/s with samples particle size ranging between 5 and 50 mm. These conditions permit the production of solid, liquid and gaseous products in significant proportions.

The work of Pan et al. [29] illustrates this type of process. In this paper a fixed bed reactor designed as experimental apparatus is used for slow pyrolysis of *Nannochloropsis* sp. The schematic diagram of the reactor is shown in Fig. 1. Nitrogen as a carrier gas was supplied to the reactor from the inlet located in the top of the reactor and its flow rate was controlled by a flow meter. A condenser (ice trap) connected at the exit of the reactor was used to collect the liquid products. The direct pyrolysis of *Nannochloropsis* sp. residue was performed in the fixed bed reactor mentioned above. The material was heated by an electric furnace with a heating rate of 10 °C/min from room temperature to the final temperature, and then kept for 2 h at the final temperature. The volatiles produced in the pyrolysis process were swept out by the carrier gas with a flow rate of 30 ml/min.

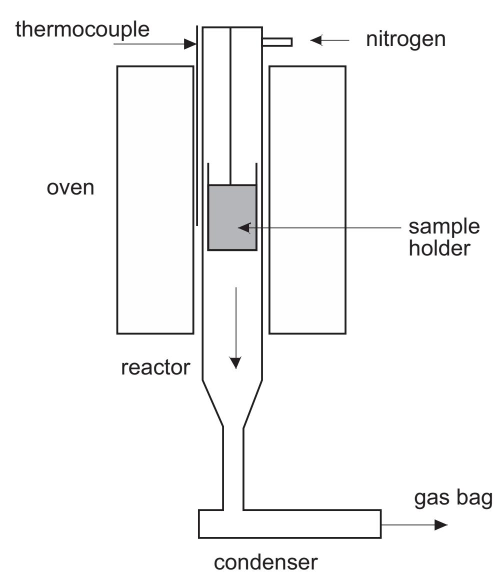


Fig. 1. The schematic diagram of the fixed bed reactor for slow pyrolysis of *Nannochloropsis* sp. (Pan et al. [29]).

Table 1
Operating parameters and expected yields for pyrolysis processes (modified from Brennan and Owende, 2010).

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Flash pyrolysis	Moderate temperature (500 °C), short residence time (about 1 s)	75	2	13
Fast pyrolysis	Moderate temperature (500 °C), moderate residence time (about 10–20 s)	50	20	30
Slow pyrolysis	Low temperature (400 °C), very long residence time (more than 30 min)	30	35	35

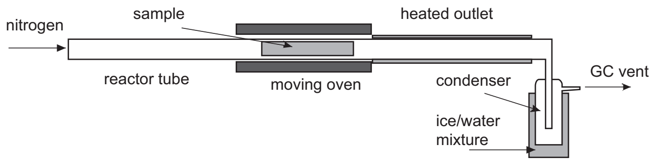


Fig. 2. Experimental set-up for fast pyrolysis of algae samples (Babich et al. [31]).

2.1.2. Fast pyrolysis

If the aim is the production of mainly liquid and/or gaseous products, a fast pyrolysis is recommended. The achievement of heating rates between 1 and 200 °C/s requires high operating temperatures, very short contact times and very fine particles (< 1 mm).

Various reactors like entrained flow reactor, wire mesh reactor, vacuum furnace reactor, vortex reactor, rotating reactor, fixed-bed reactor, circulating fluidized bed reactor, etc. were designated for performing fast pyrolysis [30].

Babich et al. [31] used a fixed-bed reactor for fast pyrolysis of the microalgae Chlorella. A schematic diagram of the experimental set-up is given in Fig. 2. An electrical oven was preheated to the desired pyrolysis temperature (300, 350, 400 or 450 °C) and moved over the reactor to start the pyrolysis of the samples. The temperature in the reactor was measured with a thermocouple placed inside the bed. The bed temperature reached the oven temperature within 3 min, involving a heating rate in the range of 1.5–2.5 °C/s.

2.1.3. Flash pyrolysis

Flash pyrolysis gives mostly liquid products due to the high heating rate (> 1000 °C/s). This requires special reactor configuration in which biomass residence times are only of few seconds. Two appropriate designs are the entrained flow reactor and the fluidized bed reactor. In addition, as flash pyrolysis requires a rapid heating, the particle size should be fairly small (< 0.2 mm). It is deemed to be a viable technique for future replacement of fossil-fuels with biomass derived liquid fuels [32] mainly because of the high biomass-to liquid conversion ratio (95.5%) that can be achieved [33]. However, there are technical challenges to be solved since pyrolysis oils are acidic, unstable, viscous, and contain solids and chemically dissolved water [34]. Therefore, the process oil will require upgrading hydrogenation, catalytic cracking to lower oxygen content and removing alkalis [35].

2.2. Pyrolysis of microalgae

The use of microalgae as feedstock for pyrolysis has many advantages over other renewable and conventional energy sources, such as, saving arable lands and stabilizing effective supply of food.

Compared to other conversion technologies, research on pyrolysis of algal biomass is quite extensive and has achieved reliable and promising outcomes that could lead to commercial exploitation [36]. Pyrolysis of several algal species have been tested, including *Chlorella* [33,37–40], salt-water *Tetraselmis* [37,41] and *Nannochloropsis residue* [29]. As an example of the results obtained (Table 2), Miao et al. [39] achieved bio-oil yields of 18% (High heating value (HHV) of 30 MJ/kg) and 24% (HHV of 29 MJ/kg) with fast pyrolysis of *Chlorella prothothecoides* and *Microcystis aeruginosa* grown phototrophically, respectively. Miao and Wu [39] used fast pyrolysis to enhance oil yield from microalgae *C. prothothecoides* after manipulating its metabolic pathway towards heterotrophic growth. The recorded oil yield of 57.9% dry wt. basis from heterotrophic cultivation (HHV of 41 MJ/kg) was 3.4 times higher than that achieved by phototrophic cultivation and the results suggest that pyrolysis has potential in algal biomass to liquids conversion.

2.3. Microwave assisted pyrolysis

Microwave-assisted pyrolysis (MAP) is a relatively new technique that has been developed and investigated in recent decades. This process offers several advantages over traditional processes, including uniform internal heating of large biomass particles, ease control, and no need for agitation or fluidization, and hence less particles (ashes) in the bio-oil.

However, to date, there are few reports on the microwave-assisted pyrolysis of microalgae. Du et al. [42] conducted MAP of *Chlorella* sp. under different microwave power levels. A schematic diagram of the system is shown in Fig. 3. They concluded that the microwave power of 750 W was the optimum value as the maximum bio-oil yield of 28.6% was obtained, the algal bio-oil exhibit a better quality than lignocellulosic bio-oils in terms of physical and chemical properties since the algal bio-oil was characterized by a low oxygen content with aliphatic and aromatic hydrocarbons constituting 22.18% of the total ion chromatogram of GC–MS. However, further upgrading to remove N and O from bio-oil is necessary to make it suitable as engine fuels. Hu et al. [43] investigated the microwave-assisted pyrolysis of *Chlorella vulgaris* under different microwave power levels, catalysts and contents of activated carbon and solid residue. In this study, the microwave power of 1500 W and 2250 W were found to be optimal for obtaining the maximum bio-oil yield of 35.83% and the maximum bio-fuel yield of 74.93%, respectively. The research indicated that the maximum temperature rising rate and pyrolysis temperature became higher as the microwave power increased. Furthermore, it has been shown that the pyrolysis reaction can be enhanced by mixing *C. vulgaris* with catalysts. Under this study, activated carbon exhibited the best catalysis action followed by the solid residue.

2.4. Hydropyrolysis

Hydropyrolysis refers to pyrolysis assisted by high hydrogen pressure (> 10 MPa). Hydropyrolysis is a pyrolysis technique that, compared to conventional pyrolysis procedures, gives rise to much higher yields of hydrocarbons with much better structural preservation. Bennett et al. [44] reported a detailed investigation of the nitrogen compounds released by hydropyrolysis of the macromolecular material of algae, bacteria, archaea and recent sediments (Priest Pot, UK; Lake Pollen, Norway). A schematic representation of the hydropyrolysis apparatus is shown in Fig. 4. Love et al. [45] evaluated (i) if the distributions of the hydrocarbon products released by hydropyrolysis from cultured cells were sufficiently distinct to act as molecular fingerprints for different classes of microorganisms; (ii) if the detail of molecular information in hydrocarbon products, in terms of retention of biologically-inherited structural and stereochemical features, was high or whether thermal cracking and isomerization were particularly problematic. They found that the hydropyrolysis can serve as a useful screening tool for identifying whether a particular biomarker structure has the potential to be used as a source-specific molecular marker or whether it has a wider taxonomic distribution. Unequivocal assignment of the biological origin of lipid compounds is of fundamental importance for improving our overall understanding of biomarker records in the natural environment and geological record.

Table 2
Current research of typical thermochemical conversion technologies applied to microalgae.

Reference	Technology	Feedstock	Conditions	Main conclusions
Minowa et al. [55]	Hydrothermal liquefaction	*Dunaliella tertiolecta*	100 ml stainless steel autoclave with a magnetic stirrer, 20 g microalgae paste (78.4% water), Na_2CO_3 (0–5% of the dry sample), nitrogen, initial pressure 3 MPa, 250–340 °C, 5–60 min	Maximum bio-oil yield (43.8%) (300 °C, 5 min, 0% Na_2CO_3) Heating value (34.0 MJ/kg) Maximum heating value (37.8 MJ/kg) (340 °C, 5 min, 0% Na_2CO_3). Bio-oil yield (42.6%)
Shuping et al. [56]	Hydrothermal liquefaction	*Dunaliella tertiolecta*	100 ml stainless steel autoclave with a magnetic stirrer, 7 g sample, 70 ml distilled water, 0–10% Na_2CO_3 (catalysts), 280–380 °C, 10–90 min.	Maximum bio-oil yield (25.8%) (360 °C, 50 min, 5% Na_2CO_3) Heating value (30.74 MJ/kg)
Brown et al. [54]	Hydrothermal liquefaction	*Nannochloropsis* sp.	35 ml stainless-steel reactor, 4.27 g microalgae paste (79% water), 200–500 °C, 60 min	Highest bio-oil yield (43%) (350 °C) Heating value (39 MJ/kg)
Jena et al. [51]	Hydrothermal liquefaction	*Spirulina platensis*	1.8 l reactor with impeller agitation (300 rpm), 500–750 ml premixed algal slurry (10–50% solids), 200–380 °C, 0–120 min, nitrogen, initial pressure 2 Mpa	Biocrude obtained at 350–380 °C had fuel properties similar to that of petroleum crude and could be further refined to a liquid transportation fuel. Maximum bio-oil yield (39.9%) (350 °C, 60 min, 20% solids)
Vardon et al. [52]	Hydrothermal liquefaction	Spirulina, swine manure and digested anaerobic sludge	2 l reactor, 800 g slurry (80% water), nitrogen, initial pressure 0.65 Mpa, 300 °C, 30 min	Feedstock organic content and nutritional composition greatly affect hydrothermal liquefaction biocrude oil yields and chemistry, despite having similar bulk elemental distributions.
Biller and Ross [53]	Hydrothermal liquefaction	Model biochemical components, *Chlorella vulgaris*, *Nannochloropsis oculata*, Porphyridium cruentum and Spirulina	75 ml reactor, 3 g sample, 27 ml distilled water, 1 M Na_2CO_3 or 1 M HCOOH, 350 °C, 1 h	Bio-oil formation follows the trend lipids > proteins > carbohydrates. Proteins and lipids were converted to oil most efficiently without catalysts while carbohydrates were best processed using Na_2CO_3. Biochemical components behave additively for some microalgae but not for others. Oil is generated from each biochemical component.
Vardon et al. [50]	Hydrothermal liquefaction Slow pyrolysis	Scenedesmus raw and defatted and Spirulina	500 ml reactor, 250 g biomass slurry (80% moisture), 300 °C, 30 min 100 g sample, 450 °C, 50 °C/min, 2 h, nitrogen, 100 ml/min	Hydrothermal liquefaction and slow pyrolysis produced bio-oils with similar heating value (36 MJ/kg moisture-free). Pyrolysis bio-oils displayed a higher percentage of cyclic oxygenates and lower molecular weight and boiling point distributions.
Peng et al. [40]	Slow pyrolysis	*Chlorella protothecoides*	5.5 ml stainless steel autoclave, 1 g sample, 200–600 °C, 5–120 min	Maximum oil yield (52%) (500 °C, 5 min)
Grierson et al. [37]	Slow pyrolysis	*Tetraselmis chui*, Chlorella like, *Chlorella vulgaris*, Chaetocerous muelleri, *Dunaliella tertiolecta*, Synechococcus	100 mg sample, maximum temperature of 750 °C, 10 °C/min, helium, 50 ml/min	Maximum liquid percentage (43%) (*T. chui*, 500 °C)
Pan et al. [29]	Slow pyrolysis	*Nannochloropsis* sp. residue after lipid extraction	1 g sample, HZSM-5/sample (0/1–1/1), 300–500 °C, 10 °C/min, 2 h, nitrogen, 30 ml/min	Maximum bio-oil yield (31.1%) (400 °C, 0/1). The yield gradually decreased as the catalyst-to-sample ratio increased. Compared to bio-oil from direct pyrolysis, bio-oil from catalytic pyrolysis had lower oxygen content and higher heating value (32.2 MJ/kg).
Grierson et al. [41]	Slow pyrolysis	*T. chui*	Fixed bed infrared pyrolysis oven, 2.4 g sample, maximum temperature of 500 °C, 20 min, 10 °C/min, helium, 50 ml/min.	The pyrolytic oil fraction exhibits a wide variety of fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidines, phytol and phenols, with a high heating value (HHV) of 28 MJ/kg. The biochar produced has a HHV of 14.5 MJ/kg and high cation exchange capacity and large concentration of N.
Miao et al. [39]	Fast pyrolysis	*C. protothecoides* and *Microcystis aeruginosa*	Fluid bed reactor, 4 g/min, 200 g sample, 500 °C, 600 °C/s, nitrogen, 0.4 m^3/h, vapor residence time (2–3 s)	Bio-oil from fast pyrolysis of microalgae has a higher HHV (29 MJ/kg), which is about 1.4 times of that of wood. Furthermore, the lower oxygen contents of microalgae make them have better storage stability.
Miao and Wu [38]	Fast pyrolysis	*C. protothecoides*	Fluid bed reactor, 4 g/min, 200 g sample, 400–600 °C, 600 °C/s, nitrogen, 0.4 m^3/h, vapor residence time (2–3 s)	Maximum bio-oil yield (57.9%) (450 °C) produced from heterotrophic cells was 3.4 times higher than from autotrophic cells by fast pyrolysis. Additionally, it has a much lower oxygen content, a higher heating value (41 MJ/kg), a lower density (0.92 kg/l) and a lower viscosity (0.02 Pa s).
Du et al. [42]	Microwave-assisted pyrolysis	Chlorella sp.	30 g sample, 6 g solid char (catalyst), 500–1250 W (462–627 °C), 20 min, nitrogen, 500 ml/min	Maximum bio-oil yield (28.6%) (750 W). Algal bio-oil (low oxygen content) exhibited a better quality than lignocellulosic bio-oils.
Hu et al. [43]	Microwave-assisted pyrolysis	*Chlorella vulgaris*	30 g sample, 750–2250 W, 5% catalysts (activated carbon, CaO, SiC and solid residue), activated carbon and solid residue (5, 10, 20, 30%), nitrogen, 300 ml/min	Maximum bio-oil yield (35.83%) (1500 W). Catalysts enhanced the production of gas. Activated carbon was the best among the tested.

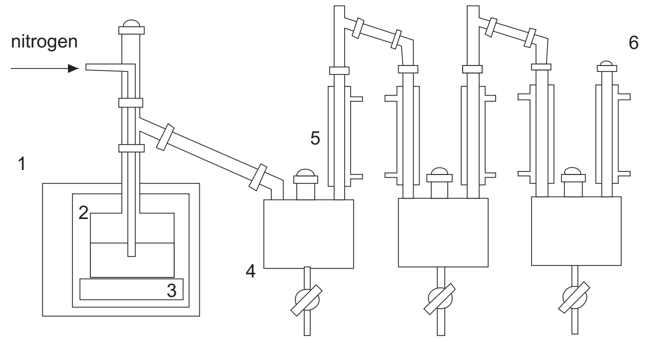


Fig. 3. The schematic diagram of MAP system: (1) microwave cavity; (2) quartz reactor; (3) holder; (4) bio-oil collector; (5) condensers; (6) gas sampling [42].

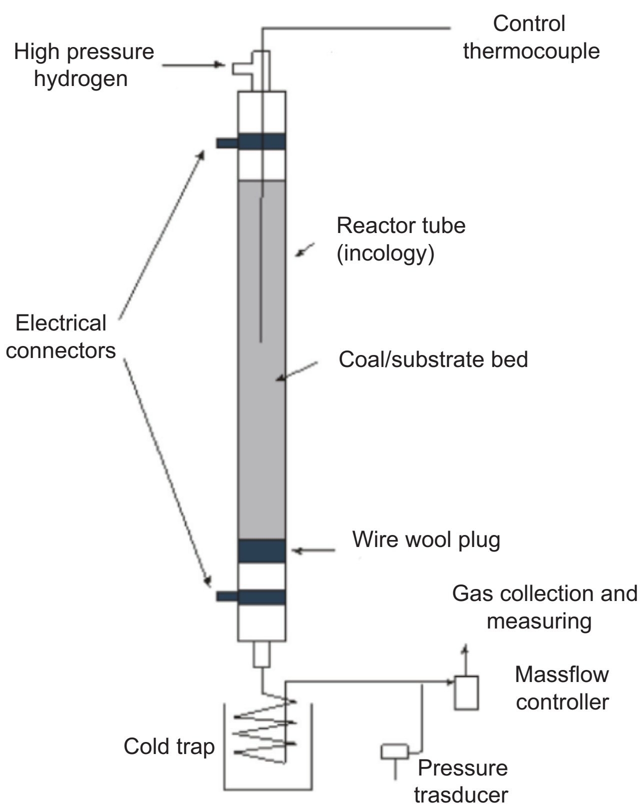


Fig. 4. Schematic representation of the hydropyrolysis apparatus [78].

3. Hydrothermal liquefaction

All these different forms of pyrolysis use dry microalgae feedstock, and therefore require a previous drying step, that has an impact on the economic and energetic yield of the global process. In contrast, one of the advantages of the hydrothermal liquefaction, also known as thermochemical liquefaction, supercritical water gasification or hydrous pyrolysis, is that it does not require such step. Sawayama et al. [46] described the method of calculating the energy required for liquefaction and concludes that energy requirements for algae liquefaction is 6.69 MJ/kg of oil produced under the assumptions of organic content 50%, oil yield 64%, heating value 45.9 MJ/kg, specific heat of water 4.18 kJ/kg K and heating value of solids 1.25 kJ/kg K. Jena et al. [47] stated that if pyrolysis were used as a conversion method, all the water should be evaporated, thus consuming the latent heat of vaporization of water 2260 kJ/kg. This means (according to Sawayama et al. [46]), that the consumption of 28.25 MJ/kg of oil for evaporating the water from a sample containing 80% water.

Hydrothermal liquefaction can be considered as a pressurized aqueous pyrolysis since hydrothermal liquefaction typically uses a feedstock with a moisture content of approximately 80%. Although it has the advantage of converting wet biomass into energy, reactors for thermochemical liquefaction and fuel-feed systems are complex and therefore expensive, and the heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling [48].

The process utilizes temperatures between 200 and 360 °C and pressures high enough to keep the water in the liquid phase [4]. Reaction times usually range between 5 and 60 min. Under these conditions, the biomacromolecules in the microalgae break down to form a bio-oil and gases, and as it occurs in the case of the hydropyrolysis the bio-oil obtained has a lower oxygen content, being therefore more compatible with petroleum products.

Several studies have investigated the characteristics of algal biomass as a feedstock for hydrothermal liquefaction, including *Scenedesmus* [49,50], *Spirulina* [49,51,52], *Nannochloropsis* [53]; *Chlorella* [49,53,54], *Dunaliella* [55,56] and *Botryococcus braunii* [57]. A schematic layout of the hydrothermal liquefaction process is shown in Fig. 5. As an example of the results obtained in these studies (Table 2), Dote et al. [57] successfully used thermochemical liquefaction at 300 °C on *B. braunii* to achieve a maximum yield of 64% dry wt. basis of oil with HHV of 45.9 MJ/kg and also declared a positive energy balance for the process (output/input ratio of 6.67:1). In a similar study, an oil yield of 42% dry wt. was obtained from *Dunaliella tertiolecta* giving a HHV of 34.9 MJ/kg and positive energy balance of 2.94:1 [55]. Moreover, Jena et al. [51] compared the pyrolysis of *Spirulina platensis* with its hydrothermal liquefaction and they concluded that from the point of view of process

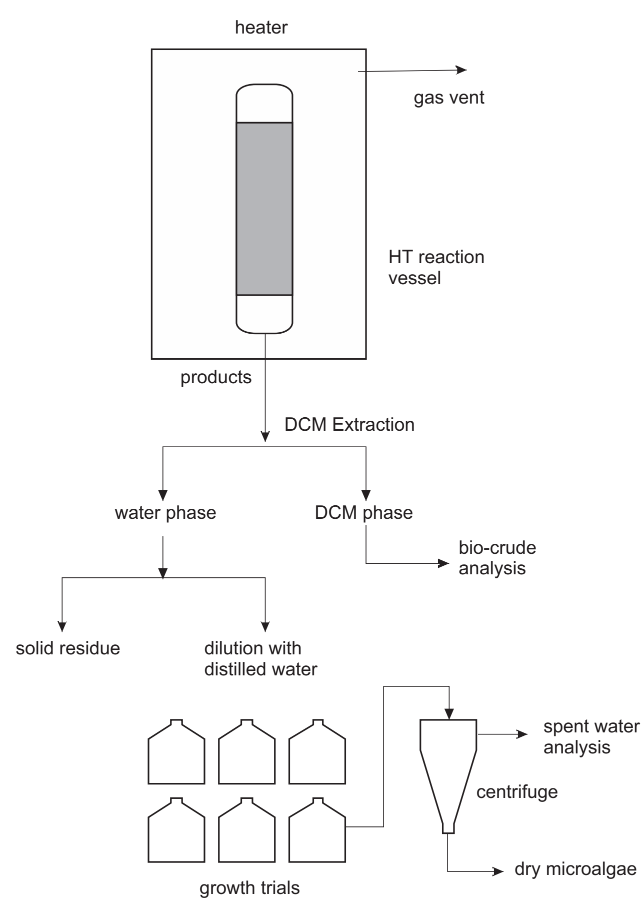


Fig. 5. Schematic layout of the hydrothermal liquefaction (HTL) process. (DCM = dichloromethane) [49].

yield, fuel quality, and energy consumption ratios, the hydrothermal liquefaction process is better for thermochemical conversion of algal biomass to liquid bio-oil than pyrolysis. These results indicate that thermochemical liquefaction is a viable option for the conversion of algal biomass-to-liquid fuel.

Another interesting point of hydrothermal liquefaction, which is being studied lastly [47,49], is that the water phase is high in all required nutrients for algae growth, so it can be used, after heavy dilution to avoid the effect of growth inhibitors such as phenols, fatty acids and nickel. Biller et al. [50] observed that *C. vulgaris*, *Scenedesmus dimorphus* and the cyanobacteria *S. platensis* and *Chlorogloeopsis fritschii* were able to grow in the recycled water but different optimum dilutions were observed. Additionally, all strains were able to use acetate, obtained in the process, as a substrate for mixotrophic growth and ammonium as a source of nitrogen.

4. Analytical applications

Pyrolysis could also have a great potential for the characterization of the microalgae and it could be used as a rapid test to obtain an idea of their biochemical composition.

4.1. Thermogravimetric analysis (TGA)

On the one hand, thermogravimetric analysis (TGA) is one of the techniques more widely used to study pyrolysis reactions that involve a solid. It allows the measurement of a wide variety of properties, such as thermal stability, moisture and volatile matter content, and, sometimes, the composition of multicomponent systems. Although, the most important signals that are obtained from TGA while the sample is being analyzed are the weight, the weight loss rate (i.e. differential thermogravimetry) and the temperature. A differential thermogravimetry curve (DTG) is obtained as the first derivative of the mass respect to the temperature or the time. This curve can be used to obtain qualitative and quantitative information of the sample composition. A qualitative analysis of the curve allows obtaining the “fingerprint” of the material and the distinction between two or more overlapped reactions and a quantitative analysis and the temperature at which the maximum mass loss occurs.

TGA has been frequently employed in literature to study the thermal decomposition of different microalgae. The pyrolysis of microalgae is usually divided in three stages. The first stage occurs between room temperature and 200 °C. During this stage, some internal rearrangement, such as water elimination, bond breakage, appearance of free radicals and formation of carbonyl and carboxyl groups takes place. The second stage of the solid decomposition takes places until approximately 500 °C depending on the microalgae and corresponds to the main pyrolysis process. It proceeds with a high rate and leads the formation of the pyrolysis products. During the third stage, the char decomposes at a very slow rate and carbon-rich residual solid forms [58]. More specifically, Pane et al. [59] studied the effects of temperature on the marine planktonic alga *Tetraselmis Suecica* by TGA in air atmosphere, reporting the existence of marked differences related to the presence of different molecules being produced during the algal growth and to the differences in the thermal properties of such molecules. According to these authors, the first of the three weight loss stages reported occurs in the range of 40–180 °C and corresponds to the loss of free water and the water loosely bound to biomolecules. In this process, the cell structure is progressively destroyed, and the alteration of lipid structures and protein thermal unfolding may occur. The second step, occurring in the 180–400 °C range, involves the decomposition of proteins and carbohydrates. This step produces the main weight loss. Finally, the third step occurs in the 400–760 °C range and corresponds to the complete oxidation of the organic matter. Similarly, Peng et al. [25] pyrolyzed the microalgae *S. platensis* and *Chlorella protothecoides* at the heating rates of 15, 40, 60 and 80 °C/min up to 800 °C to investigate their pyrolytic characteristics. Three stages (dehydration, devolatilization and solid decomposition) appeared in the pyrolysis process. *S. platensis* devolatilized mainly at 190–560 °C and *C. protothecoides* at 150–540 °C. Likewise, Marcilla et al. [60] described three main stages in the decomposition process of the microalgae *Nannochloropsis* sp., i.e. the 25–180 °C range corresponds to dehydration, the 180–540 °C range to devolatilization and the 540–800 °C, slow solid residue decomposition from the previous step. The main step of the decomposition, the devolatilization, was actually described as a very complex process involving at least three overlapped steps, at 290, 340 and 460 °C. On the other hand, the analysis by IR spectroscopy of the gases evolved in the pyrolysis of the microalgae *Nannochloropsis* sp., showed that the peak related to the C–H absorption band, presents its maximum at 462 °C, which corresponds to the third process of the second stage, and it is more important in the microalgae than in the solid residue obtained after the lipid extraction with hexane. According to TG-FTIR experiments with some standard components [glucose (saccharide), tripalmitine (lipid) and glutamine (aminoacid)], the authors suggested that the biochemical components of the microalgae seem to be decomposed in the following order: polysaccharides, proteins and finally, lipids. Analogous results were obtained in pyrolytic studies under inert atmosphere at different heating rates for the microalgae *D. tertiolecta* [27] and *C. vulgaris* [60]. Three stages (dehydration, devolatilization and solid decomposition) appeared in the pyrolysis process and *C. vulgaris* devolatilized mainly at 250–370 °C [61], while *D. tertiolecta* at 170–370 °C [27].

4.2. Pyroprobe reactor connected to a gas chromatograph with mass spectrometer detector (Py-GC/MS)

Analytical pyrolysis has been extensively used in the bibliography to obtain information about the composition of different organic materials. For example, Fabbri et al. [9] used Py-GC/MS as a rapid analytical technique for sourcing continental organic matter in marine sediments, Nguyen et al. [12] studied the biochemical changes produced in *B. braunii* during the decomposition under oxic conditions, Çoban-Yildiz et al. [7] studied the chemical composition of black sea suspended particulate organic matter, Cejka et al. [6] used Py-GC/MS to analyze fossil organic matter from sediments, which consist of different types of algae, Derrene et al. [8] used flash pyrolysis with GC/MS to characterize intractable organic molecules in algae. Kruge et al. [11] used Py-GC/MS to study the aquatic organic matter in open water sediment samples and nitrogen compounds including pyrroles, pyridines and indoles were identified in the pyrolyzate. These compounds are characteristic pyrolysis products of proteins and degraded proteinaceous matter (in this case largely from marine algae and bacteria). Ishida et al. [10] applied reactive Py-GC to determine the lipid content and the fatty acid composition of every zooplankter individual at different algae concentration.

In relation to microalgae, Thangalazhy-Gopakumar et al. [62] used analytical pyrolysis of *C. vulgaris* in a Py/GC–MS to identify major compounds present in bio-oil with and without catalyst (H+ZSM-5). The flow diagram of reactant gas and GC carrier gas during pyrolysis (adopted from the CDS pyroprobe 5200 manual) is shown in Fig. 6.

On the other hand, Valdés et al. [63] found a clear correlation between thermogravimetric analysis and Py-GC/MS analysis and the biochemical composition of the samples in studies with the

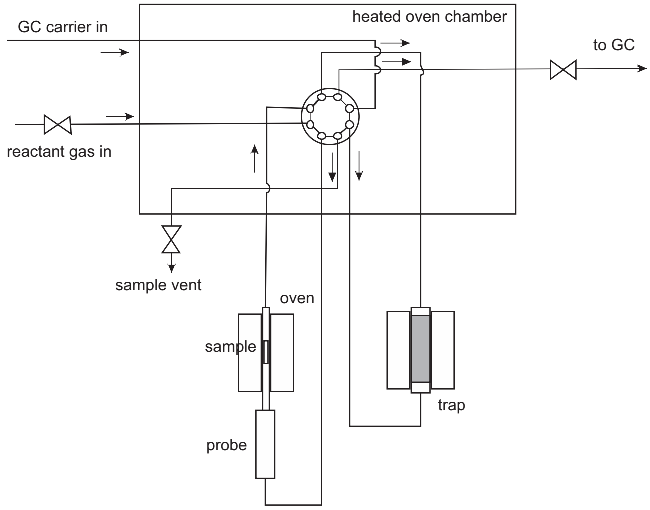


Fig. 6. Flow diagram of reactant gas and GC carrier gas during pyrolysis (adopted from the CDS pyroprobe 5200 manual).

microalgae *Nannochloropsis oculata.* In this sense both techniques, but especially the Py-GC/MS analysis has been revealed as a powerful tool for comparative purposes providing a qualitative approximation of the biochemical composition in a rapid single analysis requiring a small amount of sample.

5. Kinetic modeling of pyrolysis of microalgae

In general, providing models describing the kinetics and the governing mechanisms is very important in order to deal with the design of equipments in a thermochemical process [13]. Thermogravimetric analysis (TGA) is broadly used to determine the kinetic parameters of thermal decomposition of different materials, for example, wood [18], wheat straw, corn stalk, cotton stalk, and sorghum stalk [15], pine bark [16], grass: triple A, wheat straw, corn straw [17], cellulose, hemi-cellulose (xylan) and pectin [64–66].

However, very little information is available on kinetics of pyrolysis of microalgae [25–27], and there is not a generally accepted model that could predict the pyrolysis rate and provide a priori information about the final conversion over a wide range of culture conditions for microalgae [28].

As the decomposition reactions of microalgae usually occur following complex mechanisms, which involve diverse reactions with a different degree of overlapping, which could make difficult to elucidate whether a single or a complex process is occurring. In this case, since a complex process is occurring, it should be remarked that kinetic parameters are actually “pseudokinetic parameters”.

On the other hand, if there was a clear evidence of the existence of different processes, it might be possible to consider different steps, each one with its corresponding kinetic triplet ($f(\alpha)$, k_o, E_a).

However, when experimental results are analysed, it may be difficult to assert the number of processes involved. In this sense, it must be taken into consideration that the kinetic constants k_o and E_a should really be what their names state, i.e. constants. If contrarily, they show a dependence on conversion, it must be interpreted as evidence that a more complex mechanism is governing the process [67,68].

Despite looking really obvious, in the bibliography there is a relatively common practice consisting in concluding the kinetic analysis with figures that reveal the dependence of the activation energy on conversion degree, fact that reveals the necessity of a subsequent step in the kinetic analysis procedure to improve the proposed model, instead of constituting the final point and conclusion of the analysis.

This contradiction between what is expected (kinetic constants that should be constant) and what is possible to find in the bibliography (the dependence between kinetic constants and conversion degree), is still present in the current literature dealing with kinetic analysis.

It must be indicated that, some of the methods of kinetic analysis used date back to the beginning of the sixties, and despite the great evolution of the computers, the use of some of these procedures, that are based on rough approximations, is relatively common. Though these approximations were justifiable and useful when computational methods were not so powerful, they are now a clear nonsense.

In our opinion, and in view of the existing literature about pyrolysis of microalgae, the kinetic analysis usually exhibits some weak points that pose certain doubts on its validity. They can be summarized as:

1. The complexity of the reaction pattern is not in concordance with the complexity of the kinetic model considered.
   Isoconversional methods [69–72], useful for single step reactions, are widely applied for the kinetic analysis of microalgae (and other feedstock) thermal decomposition. However, for microalgae thermal decomposition this supposition is normally not valid. As a consequence, the activation energy obtained shows a clear dependence with the conversion degree, indicating that the process should be described in terms of multiple-step kinetics, and hence by the corresponding multiple kinetic triplets.
   Therefore, these methods would be correctly applied if the deconvolution of the specific stages was done (based e.g. on DTG curve) and the activation energy was calculated for each separate stage. Alternatively, the integration of the differential equations corresponding to kinetic models involving multiple steps to obtain the weight of the sample (or its derivative), and the minimization of the sum of the squares of the differences between the experimental and calculated weights (or weight derivatives) could also be an acceptable choice [73–76].
2. The kinetic parameters are not validated, i.e. by checking if they fit properly, or can reconstruct, the experimental kinetic curves. In a vast part of the bibliography, a kinetic analysis procedure that assumes an overall process is usually employed, while it is obvious that the decomposition pattern is complex and several processes seem to be overlapped. Nevertheless, the kinetic parameters could have a certain sense from the point of view of a pseudo kinetic analysis and they would be acceptable if they could be useful and capable of correlating the samples behaviour, at least roughly.

Thus, the recalculation of the weight loss (or conversion) curves by the suggested model, and using the kinetic parameters obtained in order to check the degree of coincidence with the raw experimental data (or alternatively the conversion profiles deduced from such experimental data) is much convenient or even necessary. Furthermore, it would permit the validity of all the assumptions involved to be checked. This aspect has already been stated in literature [76], and although it is of great importance as it is a proof of the validity of all the assumptions considered, it is rarely used or reported in bibliography dealing with kinetic analysis. The Chen et al. [77] work is one of the examples that illustrate this fact, and has been the aim of a letter to the editor [28].

Finally, it is also worth mentioning that the analysis and comparison of one single kinetic parameter (as in this case, the

activation energy) cannot be adequate, since the reaction pattern depends on the whole kinetic triplet, and it has been already demonstrated that for different activation energy values, the rest of the kinetic triplet may adopt different values to reproduce similar degradation patterns [68,75].

6. Conclusions

Hydrothermal liquefaction seems to be the most favorable and promising from the energetic point of view. Nevertheless, the residues should be recycled to improve the overall economic viability of the process. Moreover, the fuel obtained should be upgraded.

The design of pyrolysis reactors requires the employment of modelling and simulation tools, which should require an adequate kinetic analysis process. In view of the complexity of the microalgae pyrolysis pattern, the most suitable procedures would involve multi steps kinetic analysis procedures, which could permit a final verification of the model by a single comparison between experimental and calculated results.

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References

[1] Lam MK, Lee KT. Microalgae biofuels: a critical review of issues, problems and the way forward. Biotechnology Advances 2012;30:673–90.
[2] Amutio M, López G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. Resources, Conservation and Recycling 2012;59:23–31.
[3] Onay O, Gaines AF, Kockar OM, Adams M, Tyagi TR, Snape CE. Comparison of the generation of oil by the extraction and the hydropyrolysis of biomass. Fuel 2006;85:382–92.
[4] Peterson AA, Vogel F, Lachance RP, Froling M, Antal Jr. MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy & Environmental Science 2008;1(1):32–65.
[5] Xiu S, Shahbazi A, Shirley V, Cheng D. Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil. Journal of Analytical and Applied Pyrolysis 2010;88(1):73–9.
[6] Cejka J, Sobalik Z. Laboratory oxidation of fossil organic matter studied by in situ infrared spectrocopy, rock-eval pyrolysis and pyrolysis gas-chromatography-mass spectrometry. Collection of Czechoslovak Chemical Communications 1997;62:364–74.
[7] Çoban-Yildiz Y, Chiavari B, Fabbri D, Gaines AF, Galletti G, Tugrul S. The chemical composition of Black Sea suspended particulate organic matter: pyrolysis-GC/MS as a complementary tool to traditional oceanographic analyses. Marine Chemistry 2000;69:55–67.
[8] Derrene S, Largeau C, Cassadevall E. Occurrence of tightly bound isoprenoid acids in an algal, resistant biomacromolecule: possible geochemical implications. Organic Geochemistry 1991;17:597–602.
[9] Fabbri D, Sangiorgi F, Vassura I. Pyrolysis-GC–MS to trace terrigenous organic matter in marine sediments: a comparison between pyrolytic and lipid markers in the Adriatic Sea. Analytica Chimica Acta 2005;530:253–61.
[10] Ishida Y, Ohtani H, Tsuge S, Sekino T, Nakanishi M, Kimoto T. Analysis of lipid components in zooplankter individuals by reactive pyrolysis gas chromatography in the presence of organic alkali. Biological Sciences in Space 1998;12(2):131–5.
[11] Kruge MA, Mukhopadhyay PK, Lewis CFM. A molecular evaluation of contaminants and natural organic matter in bottom sediments from western Lake Ontario. Organic Geochemistry 1998;29:1797–812.
[12] Nguyen RT, Harvey HR, Zang X, van Heemst JDH, Hetényi M, Hatcher PG. Preservation of algaenan and proteinaceous material during the oxic decay of *Botryococcus braunii* as revealed by pyrolysis-gas chromatography/mass spectrometry and 13C NMR spectroscopy. Organic Geochemistry 2003;34:483–97.
[13] Koufopanos CA, Papayannakos N, Maschio G, Lucchesi A. Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects. The Canadian Journal of Chemical Engineering 1991;69:907–15.
[14] Ghetti P, Ricca L, Angelini L. Thermal analysis of biomass and corresponding pyrolysis products. Fuel 1996;75(5):565–73.
[15] Cai J, Liu R. Application of Weibull 2-mixture model to describe biomass pyrolysis kinetics. Energy & Fuels 2008;22(1):675–8.
[16] Melgar A, Borge D, Pérez JF. Estudio cinético del proceso de devolatilización de biomasa lignocelulósica mediante análisis termogravimétrico para tamaños de partícula de 2 a 19 mm. Dyna. Revista de la Facultad de Minas de la Universidad Nacional de Colombia. Sede Medellin 2008;75(155):123–31.
[17] Min F, Zhang M, Chen Q. Non-isothermal Kinetics of pyrolysis of three kinds of fresh biomass. Journal of China University of Mining and Technology 2007;17:105–11.
[18] Saddawi A, Jones JM, Williams A, Wojtowicz MA. Kinetics of the thermal decomposition of biomass. Energy & Fuels 2010;24:1274–82.
[19] Grammelis P, Basinas P, Malliopoulou A, Sakellaropoulos G. Pyrolysis kinetics and combustion characteristics of waste recovered fuels. Fuel 2009;88:195–205.
[20] Hu S, Jess A, Xu M. Kinetic study of Chinese biomass slow pyrolysis: comparison of different kinetic models. Fuel 2007;86(17–18):2778–88.
[21] Mangut V, Sabio E, Gañán J, González JF, Ramiro A, González CM, et al. Thermogravimetric study of the pyrolysis of biomass residues from tomato processing industry. Fuel Processing Technology 2006;87(2):109–15.
[22] Park YH, Kim J, Kim SS, Park YK. Pyrolysis characteristics and kinetics of oak trees using thermogravimetric analyzer and micro-tubing reactor. Bioresource Technology 2009;100(1):400–5.
[23] Vamvuka D, Kakaras E, Kastanaki E, Grammelis P. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel 2003;82(15–17):1949–60.
[24] Kirtania K, Bhattacharya S. Application of the distributed activation energy model to the kinetic study of pyrolysis of the fresh water algae *Chlorococcum humicola*. Bioresource Technology 2012;107:476–81.
[25] Peng W, Wu Q, Tu P, Zhao N. Pyrolytic characteristics of microalgae as renewable energy source determined by thermogravimetric analysis. Bioresource Technology 2001;80:1–7.
[26] Sánchez-Silva L, López-González D, Villaseñor J, Sánchez P, Valverde JL. Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. Bioresource Technology 2012;109:163–72.
[27] Shuping Z, Yulong W, Mingde Y, Chun L, Junmao T. Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer. Bioresource Technology 2010;101:359–65.
[28] García-Quesada JC, Catalá L, Marcilla A. Comments on "Thermogravimetric analysis of microalgae combustion under different oxygen supply concentrations" (Appl. Energy 88 (2011) 3189–3196). Applied Energy 2012;93:212–4.
[29] Pan P, Hu C, Yang W, Li Y, Dong L, Zhu L, et al. The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* sp. residue for renewable bio-oils. Bioresource Technology 2010;101(12):4593–9.
[30] Goyal HB, Seal D, Saxena RC. Bio-fuels from thermochemical conversion of renewable resources: a review. Renewable & Sustainable Energy Reviews 2008;12:504–17.
[31] Babich IV, van der Hulstb M, Leffertsa L, Moulijnc JA, O'Connorb P, Seshan K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. Biomass & Bioenergy 2011;35(7):3199–207.
[32] Clark JH, Deswarte FEI. Introduction to chemicals from biomass, Wiley series in renewable resources. Chichester, UK: John Wiley & Sons, Ltd; 2008.
[33] Demirbas A. Oily products from mosses and algae via pyrolysis,. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 2006;28(10):933–40.
[34] Chiaramonti D, Oasmaa A, Solantausta Y. Power generation using fast pyrolysis liquids from biomass. Renewable & Sustainable Energy Reviews 2007;11(6):1056–86.
[35] Demirbas A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Conversion and Management 2001;42(11):1357–78.
[36] Brennan L, Owende P. Biofuels from microalgae—a review of technologies for production, processing, and extractions of biofuels and co-products. Renewable & Sustainable Energy Reviews 2010;14:557–77.
[37] Grierson S, Strezov V, Ellem G, Mcgregor R, Herbertson J. Thermal characterisation of microalgae under slow pyrolysis conditions. Journal of Analytical and Applied Pyrolysis 2009;85:118–23.
[38] Miao X, Wu Q. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. Journal of Biotechnology 2004;110(1):85–93.
[39] Miao X, Wu Q, Yang C. Fast pyrolysis of microalgae to produce renewable fuels. Journal of Analytical and Applied Pyrolysis 2004;71:855–63.
[40] Peng W, Wu Q, Tu P. Effects of temperature and holding time on production of renewable fuels from pyrolysis of *Chlorella protothecoides*. Journal of Applied Phycology 2000;12:147–52.
[41] Grierson S, Strezov V, Shah P. Properties of oil and char derived from slow pyrolysis of *Tetraselmis chui*. Bioresource Technology 2011;102(17):8232–40.
[42] Du Z, Li Y, Wang X, Wan Y, Chen Q, Wang C, et al. Microwave-assisted pyrolysis of microalgae for biofuel production. Bioresource Technology 2011;102:4890–6.
[43] Hu Z, Ma X, Chen C. A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. Bioresource Technology 2012;107:487–93.

[44] Bennett B, Lager A, Russell CA, Love GD, Larter SR. Hydropyrolysis of algae, bacteria, archaea and lake sediments; insights into the origin of nitrogen compounds in petroleum. Organic Geochemistry 2004;35:1427–39.
[45] Love GD, Bowden SA, Jahnke LL, Snape CE, Campbell CN, Day JG, et al. A catalytic hydropyrolysis method for the rapid screening of microbial cultures for lipid biomarkers. Organic Geochemistry 2005;36:63–82.
[46] Sawayama S, Minowa T, Yokoyama SY. Possibility of renewable energy production and CO_2 mitigation by thermochemical liquefaction of microalgae. Biomass & Bioenergy 1999;17:33–9.
[47] Jena U, Vaidyanathan N, Chinnasamy S, Das KC. Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass. Bioresource Technology 2011;102(3):3380–7.
[48] Demirbas A. Mechanism of liquefaction and pyrolysis reactions of biomass. Energy Conversion and Management 2000;41:633–46.
[49] Biller P, Ross AB, Skill SC, Lea-Langton A, Balasundaram B, Hall C. Nutrient recycling of aqueous phase for microalgae cultivation from hydrothermal liquefaction process. Algal Research 2012;1:70–6.
[50] Vardon DR, Sharma BK, Blazina GV, Rajagopalan K, Strathmann TJ. Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis. Bioresource Technology 2012;109:178–87.
[51] Jena U, Das KC, Kastner JR. Effect of operating conditions of thermochemical liquefaction on biocrude production from *Spirulina platensis*. Bioresource Technology 2011;102(10):6221–9.
[52] Vardon DR, Sharma BK, Scott J, Yu G, Wang Z, Schideman L, et al. Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge. Bioresource Technology 2011;102:8295–303.
[53] Biller P, Ross AB. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresource Technology 2011;102(1):215–25.
[54] Brown TM, Duan P, Savage PE. Hydrothermal liquefaction and gasification of *Nannochloropsis* sp. Energy & Fuels 2010;24(6):3639–46.
[55] Minowa T, Yokoyama SY, Kishimoto M, Okakura T. Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction. Fuel 1995;74:1735–8.
[56] Shuping Z, Yulong W, Mingde Y, Kaleem I, Chun L, Tong J. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. Energy 2010;35:5406–11.
[57] Dote Y, Sawayama S, Inoue S, Minowa T, Yokoyama SY. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. Fuel 1994;73(12):1855–7.
[58] Demirbas A, Arin G. An overview of biomass pyrolysis. Energy Sources 2002;24(5):471–82.
[59] Pane L, Franceshi E, De nuccio L, Carli A. Applications of thermal analysis on the marine phytoplankton, *Tetraselmis Suecica*. Journal of Thermal Analysis and Calorimetry 2001;66:145–54.
[60] Marcilla A, Gómez-Siurana A, Gomis C, Chápuli E, Catalá MC, Valdés FJ. Characterization of microalgal species through TGA/FTIR analysis: application to *nannochloropsis* sp. Thermochimica Acta 2009;484(1-2):41–7.
[61] Bhola V, Desikan R, Santosh SK, Subburamu K, Sanniyasi E, Bux F. Effects of parameters affecting biomass yield and thermal behaviour of *Chlorella vulgaris*. Journal of Bioscience and Bioengineering 2011;111(3):377–82.
[62] Thangalazhy-Gopakumara S, Adhikaria S, Chattanathana SA, Gupta RB. Catalytic pyrolysis of green algae for hydrocarbon production using H+ZSM-5 catalyst. Bioresource Technology 2012;118:150–7.
[63] Valdés F, Catalá L, Hernández MR, García-Quesada JC, Marcilla A. Thermogravimetry and Py–GC/MS techniques as fast qualitative methods for comparing the biochemical composition of *Nannochloropsis oculata* samples obtained under different culture conditions. Bioresource Technology 2013;131:86–93.
[64] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behavior and kinetics of biomass derived materials. Journal of Analytical and Applied Pyrolysis 2002;62(2):331–49.
[65] Miller RS, Beltrán J. A generalized biomass pyrolysis model based on superimposed cellulose, hemicellulose and lignin kinetics. Combustion Science and Technology 1997;126:97–137.
[66] Stenseng M, Jensen A, Dam-Johansen K. Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry. Journal of Analytical and Applied Pyrolysis 2001;58-59(1):765–80.
[67] Conesa JA, Marcilla A, Caballero JA, Font R. Comments on the validity and utility of the different methods for kinetics analysis of thermogravimetric data. Journal of Analytical and Applied Pyrolysis 2001;58-59:617–33.
[68] Maciejewski M. Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project Ð the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. Thermochimica Acta 2000;355:145–54.
[69] Akahira T, Sunose T. Method of determining activation deterioration constant of electrical insulating materials. Report of Research Institute. Chiba Institute of Technology (Science of Technology) 1971;16:22–31.
[70] Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. Journal of Research of the National Bureau of Standards, Part A 1966;70:487–523.
[71] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. Journal of Polymer Science Part C: Polymer Letters 1964;6:183–95.
[72] Ozawa T. A new method of analyzing thermogravimetric data. Bulletin of the Chemical Society of Japan 1965;38:1881–6.
[73] Beltrán M, Marcilla A. Kinetic models for the thermal decomposition of PVC plastisols. Polymer Degradation and Stability 1997;55(1):73–87.
[74] García-Quesada JC, Marcilla A, Gilbert M. Study of the pyrolysis behaviour of peroxide crosslinked unplasticized PVC. Journal of Analytical and Applied Pyrolysis 2001;58–59:651–66.
[75] Marcilla A, Garcia-Quesada JC, Ruiz-Femenia R. Additional considerations to the paper entitled: computational aspects of kinetic analysis. Part B: the ICTAC kinetics project the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. Thermochimica Acta 2006;445: 92–8.
[76] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta 2011;520:1–19.
[77] Chen C, Ma X, Liu K. Thermogravimetric analysis of microalgae combustion under different oxygen supply concentrations. Applied Energy 2011;88:3189–96.
[78] Love GD, Snape CE, Carr AD, Houghton RC. Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis. Organic Geochemistry 1995;23(10):981–6.